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DEVELOPMENT AND VERIFICATION OF THE RELATIONSHIP
BETWEEN ATOMIC VIBRATIONAL AMPLITUDE AND
THERMAL EXPANSION OF CRYSTALLINE SOLIDS

By

Bland A. Stein

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
in candidacy for the degree of

MASTER OF SCIENCE

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ABSTRACT

The relationship between the mean square vibrational amplitude of the atoms of a crystalline solid and the thermal expansion of that solid is derived from basic principles, assuming a simple potential energy function between atoms. The functional accuracy of this relationship is proven for several cubic lattice elements and compounds by experimental data reported in the literature. The constants of the relationship are calculated for the materials investigated.

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IV. INTRODUCTION AND LITERATURE REVIEW

The energy of a solid material is composed of two factors: (1) The potential energy of the atoms due to the existence of the other atoms in the material (2) The thermal energy, which is the sum of the oscillating energies of all atoms about their equilibrium positions. Accordingly, all functions of crystalline solids can be derived, if logical potential functions between atoms and responses to deviations of atoms from equilibrium positions based on these functions are assumed. Many of these theoretical relationships were derived in the first three decades of this century. Experimental verification was impossible, however, until development of precision equipment such as stable X-ray diffraction units, equipped with modern electronic counters and both high and low temperature operational capability. This type of equipment has become commercially available only in recent years.

Specifically, the concepts which led to a relationship between the mean vibrational amplitude of the atoms in a crystal and the thermal expansion of the crystal were developed by Gruneisen in reference 1 and later reconsidered with some clarification by Roberts and Miller in reference 2. The derivation of this relationship will be presented herein in greater detail than that which is currently found in the published literature. Experimental data reported in the literature will be cited to show the functional accuracy of the relationship, and the constants of the equation for several pure metals with cubic lattice structures and four compounds with NaCl structures will be calculated.

V. LIST OF SYMBOLS

| | |
|------------------------|---|
| A | attractive constant in the relation for the potential energy of a mole of solid crystalline material |
| a | attractive constant in the relation for the potential energy of a pair of atoms |
| a_0 | lattice parameter |
| $\frac{a' - a_0}{a_0}$ | linear thermal expansion |
| B | repulsive constant similar to A |
| b | repulsive constant similar to a |
| C | constant |
| c_v | specific heat at constant volume |
| D | atomic elastic force constant |
| E | thermal energy of atomic oscillations per mole |
| F, f | force |
| F_e | free energy |
| $F(x)$ | $\log (1 - e^x)$ |
| $G(V)$ | $V \frac{d\theta_c}{dV}$ |
| $G'(V)$ | $\frac{\partial G(V)}{\partial V}$ |
| h | Planck's constant |
| I | intensity of diffracted X-rays |
| k | Boltzmann's constant |
| k' | a summation term |

| | |
|-------------------------|--|
| M | exponential factor in the Debye-Waller formula for reduction of diffracted X-ray intensity with increasing temperature |
| M_0 | atomic or molecular weight |
| m | attraction exponent in the relation for the potential energy of a pair of atoms |
| N | Avogadro's number |
| n | repulsion exponent similar to m |
| p | pressure |
| q_0 | $\frac{V_0}{r_{x_0}}$ |
| q_λ, q'_λ | summation factors |
| R | universal gas constant |
| r | distance between neighboring atoms, based on atomic volume |
| \bar{r} | mean distance between neighboring atoms |
| S | entropy |
| T | temperature |
| U | total energy per mole |
| V | volume |
| $\frac{\Delta}{V_0}$ | volume thermal expansion |
| w | number of atoms per unit cell for a specific lattice configuration |
| x_0 | compressibility at absolute zero |

| | |
|--------------------|---|
| z^2 | a factor in the relationship between vibrational amplitude and thermal expansion which depends on the potential function under consideration |
| γ | Grüneisen's constant |
| Δ | $V - V_0$ |
| δx | small atomic displacement from mean position |
| ξ | $\frac{h\nu}{kT}$ |
| η | weight of one atom |
| Θ | Debye characteristic temperature |
| θ | Bragg diffraction angle |
| θ_1 | angle between the direction of atomic displacement and the line between atoms of an atomic pair |
| θ_2 | angle of the line between atoms after the displacement, δx , relative to its position before displacement, when $\theta_1 = 90^\circ$ |
| λ_1 | frequency of X-radiation used for diffraction study |
| $\overline{\mu^2}$ | mean square vibrational amplitude |
| ν | frequency of atomic vibrations |
| ν_c | Debye frequency |
| ν_λ | the specific number of atoms separated from a given atom by the distance $k'r_0$ in a specific lattice configuration |
| σ | a lattice sum |
| Φ | total potential energy of the atoms of a mole of crystalline material |

- ϕ_c ϕ minus the potential energy of oscillation
- ϕ potential energy of a pair of atoms
- ϕ_{A_0} attractive potential energy of a single atom due to the other atoms in a mole of the material
- ϕ_{R_0} repulsive potential energy similar to ϕ_{A_0}
- $\phi(x)$ the Debye function: $\phi(x) = \frac{3}{x^2} \int_0^x \frac{\xi}{e^\xi - 1} d\xi$
- $\psi(m), \psi(n)$ lattice sums for attractive and repulsive terms, respectively, which depend only on the form of the lattice and the potential law between the atoms

Subscripts:

- o absolute zero conditions, $T = 0$, $p = 0$
- o' room temperature value
- T any specific temperature other than zero
- λ index of summation for the lattice sums

VI. QUALITATIVE RELATIONSHIPS

The potential energy of a pair of atoms includes two terms:

(1) A repulsion term which will be predominant when the distance between the atoms is less than some equilibrium distance (2) An attraction term which will be predominant for distances greater than the equilibrium distance. A graph of the net potential energy as a function of distance between atoms will show a minimum at the equilibrium distance, r_0 , as indicated in figure 1. Since force is the negative derivative of the potential energy, the net force between the two atoms will be repulsive when the atoms are closer together than the equilibrium distance, attractive when they are farther apart than r_0 . The shapes of the curves of the repulsive and attractive forces against the interatomic distance are shown in figure 2. The net force curve is also shown. It should be noted that if the net force curve was a straight line, there would be no explanation for thermal expansion with increasing temperatures, since the equilibrium position of each atom would still be the same, even though the vibrational amplitude was increased. For the net force curve shown in figure 2, however, the force restoring the atom to its equilibrium position will be less with increasing distances between the atoms than decreasing distances, effectively increasing the mean distance between atoms with increasing vibrational amplitude. This will provide for thermal expansion when the vibrational amplitude increases with increasing temperature. The form of the relationship between vibrational amplitude and thermal expansion is considered

in the following paragraph and the specific constants of the relationship will be determined later in this thesis.

It will subsequently be shown that the relationships for the potential energy of a pair of atoms in the crystalline matrix and the potential energy of a mole of the crystalline material are of the same form. Accordingly, the curve of the potential energy of the system as a function of the mean distance between the atoms, shown in figure 3, is quite similar to the net potential energy curve of figure 1. In figure 3 it may be noted that as the temperature of the system increases from T_0 to T_1 the potential energy of the system increases, due to lattice expansion alone (considering all atoms fixed in their mean positions), from PE_{T_0} to PE_{T_1} and the mean distance between atoms increases from $\overline{r_0}$ to $\overline{r_1}$. Any displacement, δx , of an atom from its mean position at this temperature T_1 must increase the potential energy of the system according to the PE versus δx curve, which has been superimposed in figure 3 (the scale of this latter curve has been highly magnified). This PE versus δx curve is parabolic because of the argument given in appendix A, which leads to the linear relationship between the mean square vibrational amplitude, $\overline{\mu^2}$, and temperature.

It is well known that the relationship between thermal expansion and temperature is approximately linear for crystalline solids. Since the relationship between $\overline{\mu^2}$ and temperature is also approximately linear, the relationship between mean square vibrational amplitude and thermal expansion should be linear, and this will be verified herein.

VII. QUANTITATIVE RELATIONSHIPS

In accordance with the concepts discussed in the preceding section, the potential energy of two stationary atoms is given by:

$$\phi = \frac{b}{r^n} - \frac{a}{r^m} \quad (1)$$

Repulsion Attraction
term term

Appendix B presents the development which leads to the mean value of the potential energy per mole of crystalline solid.

The force between the atoms, due to the potential energy given in equation (1), is:

$$f(r) = \frac{-\partial\phi}{\partial r} = \frac{nb}{r^{n+1}} - \frac{ma}{r^{m+1}} \quad (2)$$

Referring to equations (1) and (2), n must be larger than m to meet the requirements previously stated.

Considering the force relationship of equation (2), the frequency of the atomic vibrations is derived in appendix C to be:

$$\nu^2 = \frac{z^2 N^{2/3} V_0^{1/3}}{M_0 X_0} \quad (3)$$

In appendix D, the relationship between thermal expansion and vibrational energy is shown to be:

$$\frac{\Delta}{V_0} = \frac{E}{Q_0} \quad (4)$$

The mean square vibrational amplitude of the atoms of a crystal-line monatomic solid is defined by:

$$E = \frac{8}{3} \pi^2 \nu_c^2 \mu^2 M_0$$

$$M_0 \nu_c^2 = \frac{3E}{8\pi^2 \mu^2} \quad (5)$$

and, from equation (3):

$$M_0 \nu_c^2 = \frac{z^2 N^{2/3} V_0^{1/3}}{x_0} = \frac{z^2 N^{2/3} V_0}{V_0^{2/3} x_0} = \frac{z^2 V_0}{r_0^2 x_0} = \frac{r z^2 Q_0}{r_0^2} \quad (6)$$

Combining this with equations (D-21) and (4), the relationship between the mean square vibrational amplitude, $\overline{\mu^2}$, and the thermal expansion, $\frac{\Delta}{V_0}$, becomes:

$$\overline{\mu^2} = \frac{3 r_0^2 \Delta}{8 \pi^2 r z^2 V_0} \quad (7)$$

VIII. EXPERIMENTAL DATA

Vibrational Amplitude

Relationships for the calculation of mean square vibrational amplitude from X-ray diffraction data were developed by Debye and Waller in the early part of this century. The specific equations have been given in several publications, of which reference 3 is an example.

The reduction of the intensity of scattered X-rays with increasing temperature in cubic crystals of one kind of atom is expressed by the Debye-Waller formula:

$$I_T = I_O e^{-2M} \quad (8)$$

where:

$$M = \frac{8\pi^2 \sin^2 \theta \overline{u^2}}{3\lambda_1} \quad (9)$$

M may also be expressed in terms of the Debye temperature, Θ , as:

$$M = \frac{6h^2 \sin^2 \theta}{\eta k \Theta \lambda_1} \left\{ \frac{\phi(x)}{x} + \frac{1}{4} \right\} \quad (10)$$

where $x = \Theta/T$ and $\phi(x)$ is the Debye function, defined by equation (D-3).

Solving equations (9) and (10) for the mean square vibrational amplitude, the following is obtained:

$$\overline{\mu^2} = \frac{9h^2}{4\pi^2 k \eta \Theta} \left\{ \frac{\phi(x)}{x} + \frac{1}{4} \right\} = \frac{9h^2 N}{4\pi^2 M_0 \Theta k} \left\{ \frac{\phi(x)}{x} + \frac{1}{4} \right\} \quad (11)$$

Substituting suitable values for the constants, the following equation gives $\overline{\mu^2}$ in cm^2 :

$$\overline{\mu^2} = \frac{4.364 \times 10^{-14}}{M_0 \Theta} \left\{ \frac{\phi(x)}{x} + \frac{1}{4} \right\} \quad (12)$$

Considering equation (12) it may be noted that the mean square vibrational amplitude which provides the zero point energy is:

$$\overline{\mu^2} = \frac{4.364 \times 10^{-14}}{4M_0 \Theta}, \text{ cm}^2 \quad (13)$$

In order to change the bracketed term in equation (12) into a form more easily calculated, both sides are multiplied by x/x to give:

$$\overline{\mu^2} = \frac{4.364 \times 10^{-14}}{M_0 \Theta x} \left\{ \phi(x) + \frac{x}{4} \right\}$$

$$\overline{\mu^2} = \frac{4.364 \times 10^{-14} T}{M_0 \Theta^2} \left\{ \phi(x) + \frac{x}{4} \right\}, \text{ cm}^2 \quad (14)$$

A graph of the function $\phi(x) + x/4$ versus x is given in figure 5.

Experimentally determined values of Θ at various temperatures were presented by Owen and Williams for aluminum, copper, and gold in reference 4, by Chipman for lead in reference 5, by Simerska for silver in reference 6, by Gazzara for iron in reference 7, and by Houska for tungsten, titanium carbide, zirconium carbide, titanium nitride, and

zirconium nitride in reference 8. These data are graphically presented in figure 6. Values of $\overline{\mu^2}$ calculated from these data using equation (14) are given in table I and figure 7. From extrapolation of the data in figure 6 to 0° K, zero point mean square vibrational amplitudes were calculated using equation (13) and are also given in table I and figure 7. It should be noted that the data for the compounds assumes equal amplitudes for both kinds of atoms, which was shown in reference 8 to be a good approximation.

Thermal Expansion

Experimentally determined values of linear thermal expansion at various temperatures are given in reference 9 for aluminum, silver, gold, iron, copper, and tungsten, in reference 10 for lead and in reference 8 for titanium carbide, titanium nitride, zirconium carbide, and zirconium nitride. The variation of thermal expansion with temperature for these materials is shown in figure 8.

IX. RESULTS AND DISCUSSION

Using the values of mean square vibrational amplitude from table 1 and thermal expansion from figure 8, the variation of $\overline{\mu^2}$ with the product of linear thermal expansion and r_0^2 is shown in figure 9 for the materials considered herein. Values of the lattice parameter, a_0' , used to calculate r_0 from equation (B-2), were obtained from references 8 and 11. For isotropic materials:

$$\frac{\Delta}{V_0} = \frac{(a' - a_0')}{a_0'} \quad (15)$$

so that equation (7) can be written:

$$\overline{\mu^2} = \frac{9r_0^2(a' - a_0')}{8\pi^2\gamma z^2 a_0'} \quad (16)$$

Calculations of the factor z^2 were made from the slope of the lines of figure 9, using equation (16) and values of γ from reference 1. These values of z^2 are listed in table 2. Although room temperature values of the lattice parameter and linear thermal expansion based on room temperature data were used in the calculations when the relation is based on absolute zero values, the errors in the z^2 values due to these substitutions will not be substantial and may be considered insignificant for the purposes of this study.

Of considerable significance in these results is the fact that the curves of figure 9 are straight lines for all the elements and compounds

considered herein. This proves the functional accuracy of equation (7), which was evolved from basic principles concerning the energy functions of crystalline solids.

X. CONCLUSIONS

The functional accuracy of equation (7), derived herein from basic principles, is proven for various cubic lattice elements and compounds by the experimental data cited. The use of the calculated values of the constant of the equation, z^2 , to determine the constants of the potential energy function for the atoms of crystalline solids cannot be attempted until more data is available for values of some of the constants or until a potential function with fewer constants can be considered.

XI. ACKNOWLEDGMENT

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XII. VITA

The author was born in New York City on February 27, 1934. He attended public schools in the Bronx, New York, and was graduated from The William Howard Taft High School in June of 1951. He entered The College of The City of New York in September of 1951, and received the degree of Bachelor of Mechanical Engineering in February 1956. From that time to the present, the author has been employed by the National Aeronautics and Space Administration (formerly the National Advisory Committee for Aeronautics) at Langley Air Force Base, Hampton, Virginia.

XIII. REFERENCES

1. Grüneisen, E.: The State of Solids, Handbuch der Physik, Vol. 10, p. 1, (1926)
2. Roberts, J. K., and Miller, A. R.: Heat and Thermodynamics, Interscience Publishers, New York, Fifth Edition, (1960)
3. Lonsdale, K.: Acta Cryst., Vol. 1, p. 142, (1948)
4. Owen, E. A., and Williams, R. W.: Proc. Roy. Soc., Vol. A188, p. 509, (1947)
5. Chipman, D. R.: Temperature Dependence of the Debye Temperatures of Aluminum, Lead and Beta Brass by an X-ray Method, MRL Rep. No. 67, Watertown Arsenal, Mass., Oct. 1959
6. Simerska, M.: Acta Cryst., Vol. 14, p. 1259, (1961)
7. Gazzara, C. P.: Debye Temperature of Carbonyl Iron, U. S. Dept. Comm. Off. Tech. Serv. P. B. Rept. 146,161, WAL TR-805, (1960)
8. Houska, C. R.: Thermal Expansion and Atomic Vibration Amplitudes for TiC, TiN, ZrC, ZrN, and Pure W, to be published in Phys. Chem. Solids in 1964.
9. Goldsmith, A., Waterman, T. E., and Hirschhorn, H. J.: Handbook of Thermophysical Properties of Solid Materials, Macmillan Co., New York, (1961)
10. Hindert, P., and Sweeney, W. T.: U. S. Bur. Stds. J. Res., Vol. 9, p. 703
11. Parrish, W., and Wilson, A. J. C.: International Tables for X-ray Crystallography, Kynoch Press, Birmingham, England, (1959)

APPENDIX A

THE FORM OF THE RELATION BETWEEN VIBRATIONAL AMPLITUDE
AND POTENTIAL ENERGY OR TEMPERATURE

The average vibrational energy of a mole of crystalline solid is:

$$E = 3NkT \quad (A-1)$$

so that the average vibrational energy of each atom is:

$$E_1 = 3kT \quad (A-2)$$

Referred to any given axis, the X-axis for instance, the average vibrational energy of each atom is

$$E_{1x} = kT \quad (A-3)$$

Assuming the law of equipartition of energy to apply, the potential energy portion of the average vibrational energy expressed in equation (A-3) is $\frac{1}{2} E_{1x}$ or:

$$\langle PE_{1x} \rangle_{av} = \frac{1}{2} kT \quad (A-4)$$

This potential energy is also related to the displacement of the atom from its mean position, referred to the X-axis, δx . This relationship is:

$$PE_{1x} = \frac{1}{2} F \delta x = \frac{1}{2} D (\delta x)^2 \quad (A-5)$$

The mean square vibrational amplitude of the atoms, referred to the X-axis, $\overline{\mu_x^2}$, is the average squared displacement of the atom from its mean position, that is:

$$\langle (\delta x)^2 \rangle_{av} = \overline{\mu_x^2} \quad (A-6)$$

Substituting into the potential energy equations, the following result is obtained:

$$\begin{aligned} \langle PE_{1x} \rangle_{av} &= \frac{1}{2} D \langle (\delta x)^2 \rangle_{av} = \frac{1}{2} D \overline{\mu_x^2} = \frac{1}{2} kT \\ \overline{\mu_x^2} &= \frac{k}{D} T \end{aligned} \quad (A-7)$$

which shows the linear relationship between $\overline{\mu^2}$ and potential energy and between $\overline{\mu^2}$ and temperature.

APPENDIX B

POTENTIAL ENERGIES AND FORCES

The potential energy of a pair of atoms is given by:

$$Q = \frac{b}{r^n} - \frac{a}{r^m} \quad (1)$$

Repulsion Attraction
term term

Consider a solid under zero external pressure ($p = 0$) and at a temperature of absolute zero ($T = 0$). Neglecting the small vibrational amplitude at absolute zero, it can be assumed that the atoms are at rest in their equilibrium positions. For these conditions, the volume occupied by a mole of the solid is:

$$V_0 = N r_0^3 \quad (B-1)$$

Values of r_0 can be calculated from tabulated values of lattice parameters by the following relationship:

$$\text{Volume per atom} = \frac{a_0'^3}{w} = r_0^3$$

$$r_0 = \frac{1}{(w)^{1/3}} a_0' \quad (B-2)$$

The factor w equals 2 for the body centered cubic lattice, 4 for the face centered cubic lattice, and 8 for the NaCl lattice.

To estimate the value of the potential energy of a single atom which arises from the attractive forces of the other atoms in the lattice, note that a specific number of atoms, v_λ , will be separated from the given atom by the distance $k_\lambda' r_0$. The attractive potential energy is:

$$\varphi_{Ao} = -\frac{1}{2} a \sum_{\lambda} \frac{v_\lambda}{(k_\lambda' r_0)^m} \quad (B-3)$$

where the $\frac{1}{2}$ is the result of the consideration that each atom of a pair contains half the potential energy of that pair. The sum is taken for all values of λ so as to include all the atoms of a mole, but for all practical purposes the summation may be discontinued much sooner, when the distance outside which the atoms do not appreciably affect the potential energy of the atom in question is reached. Similarly, the potential energy of the single atom due to the repulsive forces of the other atoms in a mole of the material is given by:

$$\varphi_{Ro} = \frac{1}{2} b \sum_{\lambda} \frac{v_\lambda}{(k_\lambda' r_0)^n} \quad (B-4)$$

The factors which depend only on the nature of the lattice and on the exponents m and n can be collected, so that the following quantities can be defined:

$$\alpha_m = \sum_{\lambda} \frac{v_{\lambda}}{(k_{\lambda}')^m}, \quad \alpha_n = \sum_{\lambda} \frac{v_{\lambda}}{(k_{\lambda}')^n} \quad (\text{B-5})$$

The attractive forces are such that α_m can be accurately calculated considering only the nearest neighbor atoms. In this case a good approximation is $m = 3$. Substituting these quantities into equations (B-3) and (B-4) and adding them together, the net potential energy of the single atom becomes:

$$\phi_o = \phi_{A_o} + \phi_{R_o} = \frac{1}{2} \frac{b\sigma_n}{r_o^n} - \frac{1}{2} \frac{a\sigma_m}{r_o^m} \quad (\text{B-6})$$

The total potential energy of the atoms in the mole, at $T = 0$ and $p = 0$, is obtained by multiplying equation (B-6) by N :

$$\Phi_o = \frac{1}{2} \frac{b\sigma_n N}{r_o^n} - \frac{1}{2} \frac{a\sigma_m N}{r_o^m} \quad (\text{B-7})$$

Introducing the molar volume from equation (B-1):

$$\Phi_o = \frac{1}{2} \frac{b\sigma_n N^{n/3+1}}{v_o^{n/3}} - \frac{1}{2} \frac{a\sigma_m N^{m/3+1}}{v_o^{m/3}} \quad (\text{B-8})$$

and collecting all terms independent of volume into constants:

$$A = \frac{1}{2} a\sigma_m N^{m/3+1}, \quad B = \frac{1}{2} b\sigma_n N^{n/3+1} \quad (\text{B-9})$$

the total potential energy becomes:

$$\phi_0 = \frac{B}{V_0^{n/3}} + \frac{A}{V_0^{m/3}} \quad (\text{B-10})$$

Assume that the temperature is now raised to some value, T .

Under the previous assumptions, the separation of the atoms increases because the atoms are now oscillating about new mean positions (centers of the oscillations). The mean value of the total potential energy per mole now becomes the sum of: (a) The potential energy which the atoms would possess if they were at rest in the centers of their oscillations and (b) the mean value of the potential energy of oscillation of all the atoms. (a) is obtained directly from equation (B-10) by substituting V for V_0 :

$$\phi_c = \frac{B}{V^{n/3}} + \frac{A}{V^{m/3}} \quad (\text{B-11})$$

For (b) the oscillations of the atoms are assumed to be undamped harmonic oscillations. The total energy of these oscillations can be expressed as the increase of energy per mole when a solid is heated from absolute zero to the temperature, T , at constant volume:

$$E = \int_0^T c_v dT \quad (\text{B-12})$$

The energy of the oscillation is half kinetic and half potential (equipartition of energy), so that the potential energy of the oscillation is $\frac{1}{2} E$ and the mean value of the total potential energy per mole is:

$$\Phi = \frac{B}{v^{n/3}} - \frac{A}{v^{n/3}} + \frac{1}{2} E \quad (B-13)$$

APPENDIX C

FREQUENCY OF ATOMIC VIBRATIONS

The frequency of the atomic vibrations can be calculated from the restoring force on an atom which is displaced from its mean position in the lattice. For simplification, it will be assumed that one atom, P, is displaced and that all other atoms are at rest in their mean positions. This situation is illustrated in figure 4.

The atom P is displaced by a small distance, δx , to position Q. Consider the effect of the displacement on the force exerted on P by atoms A and B. The distances between atoms are $AP = r$, $BP = r$, $AQ = r + x \cos \theta_1$, $BQ = r - x \cos \theta_1$. If the repulsive force between any two atoms is $f(r)$, then the force due to atom A on atom P, when it is at Q, is $f(r + x \cos \theta_1)$ along the line AQ, or $f(r + x \cos \theta_1) \cos \theta_1$ in the direction PQ. If the same force convention is used, then the force due to B on P, at Q, is $-f(r - \delta x \cos \theta_1) \cos \theta_1$ in the direction PQ. The total force on atom P due to atoms A and B is:

$$F_{AB,P} = \cos \theta_1 \left\{ f(r + \delta x \cos \theta_1) - f(r - \delta x \cos \theta_1) \right\} \quad (C-1)$$

When δx is small, each force function in the above can be approximated by the first two terms of a Taylor series:

$$f(r + \delta x \cos \theta_1) = f(r) + \delta x \cos \theta_1 \frac{\partial f(r)}{\partial r} \quad (C-2)$$

Using this approximation, equation (C-1) becomes:

$$\begin{aligned}
 F_{AB,P} &= \cos \theta_1 \left\{ f(r) + \delta x \cos \theta_1 \frac{\partial f(r)}{\partial r} - f(r) + \delta x \cos \theta_1 \frac{\partial f(r)}{\partial r} \right\} \\
 &= \cos \theta_1 \left\{ 2\delta x \cos \theta_1 \frac{\partial f(r)}{\partial r} \right\} \\
 &= 2 \frac{\partial f(r)}{\partial r} \delta x \cos^2 \theta_1
 \end{aligned} \tag{C-3}$$

It should be noted that any force on atom P at right angles to δx due to atoms A and B will be exactly balanced by an opposing force due to atoms D and E.

The force between two atoms was previously given by equation (2):

$$f(r) = \frac{nb}{r^{n+1}} - \frac{ma}{r^{m+1}} \tag{2}$$

so that:

$$\frac{\partial f(r)}{\partial r} = - \frac{n(n+1)b}{r^{n+2}} + \frac{m(m+1)a}{r^{m+2}} \tag{C-4}$$

Substituting this into equation (C-3):

$$F_{AB,P} = 2\delta x \left\{ \frac{m(m+1)a \cos^2 \theta_1}{r^{m+2}} - \frac{n(n+1)b \cos^2 \theta_1}{r^{n+2}} \right\} \tag{C-5}$$

This is applicable to all pairs of atoms which do not lie in the plane through P at right angles to δx . Considering atoms in this plane,

such as C and F, the force acting on atom P, at Q, in the direction PQ, due to C and F is:

$$F_{CF,P} = 2f(r)\sin \theta_2$$

$$F_{CF,P} = 2 \frac{bx}{r} f(r) \quad (C-6)$$

which, on substitution for $f(r)$, becomes:

$$F_{CF,P} = 2bx \left\{ -\frac{ma}{r^{m+2}} + \frac{nb}{r^{n+2}} \right\} \quad (C-7)$$

To obtain the total force acting on the displaced atom, the effects of all the atoms must be summed up. Considering \bar{r} to be the distance between the mean positions of two neighboring atoms in the lattice, then the distance between the λ th atom and the displaced atom is:

$$r = k_{\lambda}' \bar{r} \quad (C-8)$$

where k_{λ}' is a numerical factor. In summation then, the force due to the N atoms in a mole on the displaced atom is:

$$F = 2bx \sum_{\lambda} \left\{ \frac{q_{\lambda} m(m+1)a}{(k_{\lambda}')^{m+2} \bar{r}^{m+2}} - \frac{q_{\lambda}' n(n+1)b}{(k_{\lambda}')^{n+2} \bar{r}^{n+2}} \right\} \quad (C-9)$$

where λ has all values from 1 to $N-1$, where for all atoms which do not lie in the plane through P at right angles to δx (such as atoms A, B, D, and E):

$$q_{\lambda} = q_{\lambda}' = \frac{1}{2} \cos^2 \theta_1 \quad (C-10)$$

and where for all atoms in this plane (such as atoms C and F):

$$q_{\lambda} = -\frac{1}{2} \frac{1}{(m+1)}, \quad q_{\lambda}' = -\frac{1}{2} \frac{1}{(n+1)} \quad (C-11)$$

The factors $\frac{1}{2}$ in equations (C-10) and (C-11) result because the atoms have been considered in pairs, such as A and B, or C and F, in equations (C-5) and (C-7).

Referring to equation (C-9), the sums which depend only on the form of the lattice and the force law between the atoms but are independent of \bar{F} can be collected into the form:

$$\psi(m) = \sum_{\lambda} \frac{q_{\lambda} m(m+1)}{(k_{\lambda}')^{m+2}}, \quad \psi(n) = \sum_{\lambda} \frac{q_{\lambda}' n(n+1)}{(k_{\lambda}')^{n+2}} \quad (C-12)$$

On substituting (C-12) into equation (C-9):

$$F = 2\delta x \left\{ \frac{a\psi(m)}{\bar{r}^{m+2}} - \frac{b\psi(n)}{\bar{r}^{n+2}} \right\} \quad (C-13)$$

The restoring force, acting to return atom P from Q to its mean position, at P, is:

$$F = -D\delta x \quad (C-14)$$

So that, considering equations (C-13) and (C-14):

$$D = 2 \left\{ \frac{b\psi(n)}{r^{n+2}} - \frac{a\psi(m)}{r^{m+2}} \right\} \quad (C-15)$$

Assume that, after the displacement δx , the atom P is released from position Q. It would then vibrate with simple harmonic motion about point P, much like a weight on a spring with a spring constant equal to D. The frequency of this vibration will be given by:

$$\nu^2 = \frac{1}{4\pi^2} \frac{D}{\eta} \quad (C-16)$$

and, in this case, ν is the frequency of the atomic vibration. On substituting (C-15) into equation (C-16):

$$\nu^2 = \frac{2}{4\pi^2\eta} \left\{ \frac{b\psi(n)}{r^{n+2}} - \frac{a\psi(m)}{r^{m+2}} \right\} \quad (C-17)$$

b can be eliminated from equation (C-17) by the consideration that, at absolute zero, Φ is a minimum, so that by differentiating equation (B-7) and equating the result to 0:

$$\begin{aligned} \frac{m a \sigma_m}{r_o^m} &= \frac{n b \sigma_n}{r_o^n} \\ b &= \frac{m a \sigma_m r_o^n}{n \sigma_n r_o^m} \end{aligned} \quad (C-18)$$

On substitution:

$$\begin{aligned}
 v^2 &= \frac{2\sigma_m m a}{4\pi^2 \eta r^{m+2}} \left\{ \frac{r_0 (n-m) r^{m+2} \psi(n)}{r^{n+2} n \sigma_n} - \frac{\psi(m)}{m \sigma_m} \right\} \\
 v^2 &= \frac{2\sigma_m m a}{4\pi^2 \eta r^{m+2}} \left\{ \left(\frac{r_0}{r} \right)^{n-m} \frac{\psi(n)}{n \sigma_n} - \frac{\psi(m)}{m \sigma_m} \right\} \quad (C-19)
 \end{aligned}$$

It will subsequently be shown that the compressibility at absolute zero is:

$$x_0 = \frac{9r_0^{m+3}}{m(n-m)\sigma_m a} \quad (D-16)$$

Substituting this into equation (C-19):

$$\begin{aligned}
 v^2 &= \frac{9r_0^{m+3} 2}{4\pi^2 \eta (n-m) x_0 r^{m+2}} \left\{ \left(\frac{r_0}{r} \right)^{n-m} \frac{\psi(n)}{n \sigma_n} - \frac{\psi(m)}{m \sigma_m} \right\} \\
 v^2 &= \frac{18r_0}{4\pi^2 \eta (n-m) x_0} \frac{r_0^{m+2}}{r^{m+2}} \left\{ \left(\frac{r_0}{r} \right)^{n-m} \frac{\psi(n)}{n \sigma_n} - \frac{\psi(m)}{m \sigma_m} \right\} \\
 v^2 &= \frac{18r_0}{4\pi^2 \eta (n-m) x_0} \left\{ \frac{\psi(n)}{n \sigma_n} \left(\frac{r_0}{r} \right)^{n+2} - \frac{\psi(m)}{m \sigma_m} \frac{r_0}{r} \right\} \quad (C-20)
 \end{aligned}$$

Now, substituting the atomic volume, $V = N r^3$, and the atomic weight, $M_0 = N \eta$, into equation (C-20):

$$v^2 = \frac{18V_0^{1/3} N^{2/3}}{4\pi^2 x_0 M_0 (n-m)} \left\{ \frac{\psi(n)}{n \sigma_n} \left(\frac{V_0}{V} \right)^{\frac{n+2}{3}} - \frac{\psi(m)}{m \sigma_m} \left(\frac{V_0}{V} \right)^{\frac{m+2}{3}} \right\} \quad (C-21)$$

or:

$$v^2 = z^2 N^{2/3} \frac{V_0^{1/3}}{M_0 x_0} \quad (3)$$

where:

$$z^2 = \frac{18}{4\pi^2(n-m)} \left\{ \frac{\psi(n)}{nc_n} \left(\frac{V_0}{V} \right)^{\frac{n+2}{3}} - \frac{\psi(m)}{mc_m} \left(\frac{V_0}{V} \right)^{\frac{m+2}{3}} \right\} \quad (C-22)$$

Since (V_0/V) is always of a magnitude close to 1 for solids, z^2 may be considered independent of volume.

The frequency, v , calculated by the above method, is similar to that for an Einsteinian oscillator. A more refined treatment given by Debye considers that in a real solid, all the atoms surrounding the displaced atom are free to vibrate when the displaced atom is released. In such a case a whole spectrum of $3N$ frequencies per mole would be obtained. Further ramification of Debye theory are considered in the next section (Appendix D).

APPENDIX D

EQUATION OF STATE AND THERMAL EXPANSION

As previously considered in appendix A, the total energy per mole in the material must include both the potential energy of all the atoms in the mole, considered to be at rest in their mean positions, plus the thermal energy generated by the atomic oscillations:

$$U = \phi_c + E \quad (D-1)$$

The Debye approximation gives the following for the oscillating energy of a monatomic isotropic material:

$$E = 3RT \theta \left(\frac{\theta}{T} \right) \quad (D-2)$$

where:

$$\theta(x) = \frac{3}{x^3} \int_0^x \frac{\zeta}{e^\zeta - 1} d\zeta \quad (D-3)$$

$$\zeta = \frac{h\nu}{kT} \quad (D-4)$$

The Debye characteristic temperature is given by:

$$\theta = \frac{\nu_c h}{k} \quad (D-5)$$

where the frequency, ν_c , is approximately an upper limit of the elastic spectrum of oscillations for the material. This upper limit is attained when neighboring atoms oscillate head on with 180° phase shift.

In accordance with the preceeding, the free energy of a mole of monatomic solid, oscillating at the frequency ν_c is:

$$F_e = U - TS$$

$$F_e = \Phi_c + 3RT \left(\frac{\Theta}{T} \right) \quad (D-6)$$

where:

$$F(x) = \log(1 - e^x)$$

The equation of state can then be derived as follows:

$$p = - \left(\frac{\partial F_e}{\partial V} \right)_{T,c}$$

$$p = - \left(\frac{\partial \Phi_c}{\partial V} \right)_T - \frac{1}{\Theta} \left(\frac{\partial \Theta}{\partial V} \right)_T 3RT \left(\frac{\Theta}{T} \right) \quad (D-7)$$

or:

$$\left(p + \frac{\partial \Phi_c}{\partial V} \right) V = - \frac{\partial \log \Theta}{\partial \log V} E \quad (D-8)$$

The Grüneisen constant is defined as:

$$\gamma = - \frac{\partial \log \Theta}{\partial \log V} \quad (D-9)$$

From equation (D-9) it can be noted that γ should be approximately independent of temperature. For different elements, the Grüneisen constants are of the same order of magnitude. Although the Grüneisen constant is defined for monatomic solids, it has been found empirically that for simplest compound lattices such as the NaCl type, γ is of the same order as the mean value of γ for the monatomic elements.

On assumption of the potential function defined in equation (1) and considered in appendix A, the equation of state for isotropic monatomic solids with regular crystallization becomes:

$$\left[p + \frac{m}{3} \frac{A}{v^{\frac{m}{3}+1}} + \frac{n}{3} \frac{B}{v^{\frac{n}{3}+1}} \right] v = rE \quad (D-10)$$

or:

$$pV + G(V) = rE \quad (D-11)$$

where:

$$G(V) = \frac{V d\phi_c}{dV} \quad (D-12)$$

Expanding $G(V)$ into a Taylor series in terms of Δ , where $\Delta = V - V_0$ and V_0 is the volume at $T = 0$ and $p = 0$, gives:

$$G(V) = G(V_0) + \Delta \left[G'(V_0) \right] + \frac{\Delta^2}{2} \left[G''(V_0) \right] + \dots \quad (D-13)$$

It has already been noted that, at absolute zero, the potential energy is a minimum, so that $\frac{\partial \phi_c}{\partial V} = 0$, and, considering equation (B-10):

$$\frac{\frac{mA}{v_0^{\frac{m}{3}+1}}}{\partial v_0^3} = \frac{\frac{nB}{v_0^{\frac{n}{3}+1}}}{\partial v_0^3} \quad (D-14)$$

Therefore:

$$G'(V_0) = V_0 \frac{d^2 \phi_c}{dV_0^2} + \frac{d\phi_c}{dV_0} \quad (1)$$

$$G'(V_0) = - \frac{\frac{m}{2} \left(\frac{m}{3} + 1 \right) A}{V_0^{\frac{m}{3}+2}} + \frac{\frac{n}{2} \left(\frac{n}{3} + 1 \right) B}{V_0^{\frac{n}{3}+2}}$$

$$G'(V_0) = - \frac{m(n-m)A}{9V_0^{\frac{m}{3}+2}} \quad (D-15)$$

and:

$$G(V_0) = 0$$

The compressibility at $p = 0$ and $T = 0$ is:

$$x_0 = - \frac{1}{V_0} \left(\frac{dV}{dp} \right)_{p=0, T=0} = - \frac{V_0}{G'(V_0)} = \frac{9V_0^{\frac{m}{3}+1}}{m(n-m)A} \quad (D-16)$$

so that:

$$G'(V_0) = - \frac{1}{x_0 V_0} \quad (D-17)$$

and, by a similar analysis:

$$G''(V_0) = - \left(\frac{m+n+3}{3} \right) \frac{1}{x_0 V_0} \quad (D-18)$$

Summing up the preceeding, equation (D-13) becomes:

$$G(V) = \frac{\Delta}{x_0} \left[1 + \frac{m+n+3}{6} \frac{\Delta}{V_0} + \dots \right] \quad (D-19)$$

and, when $p = 0$, the equation of state, equation (D-11), becomes:

$$0 + G(V) = rE$$

$$\frac{\Delta}{x_0} \left[1 + \frac{m+n+3}{6} \frac{\Delta}{V_0} + \dots \right] = rE \quad (D-20)$$

Since the thermal expansion of solids is always quite small compared with 1, the term $\left[\frac{m+n+3}{6} \frac{\Delta}{V_0} + \dots \right]$ may be neglected with an error of no more than a few percent, so that:

$$\frac{\Delta}{x_0} = rE \quad (D-21)$$

Now, defining the quantity Q_0 :

$$Q_0 = \frac{V_0}{rx_0} \quad (D-22)$$

the thermal expansion becomes:

$$\frac{\Delta}{V_0} = \frac{E}{Q_0} \quad (4)$$

TABLE 1.- CALCULATED VALUES OF MEAN SQUARE VIBRATIONAL AMPLITUDE
AT VARIOUS TEMPERATURES FROM DEBYE CHARACTERISTIC TEMPERATURES

| Material (atomic weight) | T, °K | θ , °K | $\overline{\mu^2}$, cm ² |
|-----------------------------|-------|---------------|--------------------------------------|
| Al (26.97) | 0 | 415 | 0.975×10^{-18} |
| | 10 | 414 | 0.979 |
| | 100 | 408 | 1.371 |
| | 293 | 395 | 3.19 |
| | 400 | 388 | 4.42 |
| | 600 | 375 | 7.03 |
| Cu (63.54) | 0 | 323 | 0.533×10^{-18} |
| | 100 | 320 | 0.838 |
| | 293 | 314 | 2.11 |
| | 400 | 311 | 2.89 |
| | 600 | 304 | 4.49 |
| | 900 | 295 | 7.12 |
| Ag (107.88) | 0 | 211 | 0.479×10^{-18} |
| | 291 | 210 | 2.85 |
| | 352 | 203 | 3.48 |
| | 445 | 199 | 4.58 |
| | 547 | 197 | 5.73 |
| | 669 | 195 | 7.13 |
| | 763 | 194 | 8.22 |
| | 819 | 193 | 8.90 |
| | 873 | 191 | 9.71 |
| | 977 | 185 | 11.56 |
| | 1033 | 175 | 13.69 |
| Au (197.2) | 0 | 182 | 0.304×10^{-18} |
| | 100 | 180 | 0.742 |
| | 293 | 175 | 2.155 |
| | 400 | 173 | 2.97 |
| | 600 | 168 | 4.73 |
| | 900 | 162 | 7.60 |
| Fe (55.85) | 0 | 451 | 0.433×10^{-18} |
| | 98 | 446 | 0.581 |
| | 310 | 435 | 1.379 |

TABLE 1.- CALCULATED VALUES OF MEAN SQUARE VIBRATIONAL AMPLITUDE
AT VARIOUS TEMPERATURES FROM DEBYE CHARACTERISTIC TEMPERATURES -

Continued

| Material | T, °K | Θ , °K | μ^2 , cm ² |
|-----------------|-------|---------------|---------------------------|
| (atomic weight) | | | |
| Pb (207.21) | 0 | 97.5 | 0.542×10^{-18} |
| | 80 | 94 | 1.979 |
| | 205 | 87 | 5.74 |
| | 298 | 84.5 | 8.81 |
| | 385 | 79 | 13.06 |
| | 460 | 76.5 | 16.57 |
| | 480 | 75.5 | 17.77 |
| | 540 | 73 | 21.40 |
| | 570 | 71.5 | 23.20 |
| W (183.92) | 0 | 348 | 0.171×10^{-18} |
| | 298 | 345 | 0.610 |
| | 1063 | 345 | 2.100 |
| | 1373 | 342 | 2.79 |
| | 1673 | 325 | 3.73 |
| | 1953 | 338 | 4.00 |
| TiC (59.91) | 0 | 779 | 0.234×10^{-18} |
| | 298 | 766 | 0.865 |
| | 1043 | 730 | 2.86 |
| | 1373 | 780 | 3.31 |
| | 1673 | 730 | 4.58 |
| | 1933 | 695 | 5.81 |
| TiN (61.91) | 0 | 711 | 0.248×10^{-18} |
| | 298 | 700 | 0.981 |
| | 1029 | 665 | 3.28 |
| | 1284 | 665 | 4.12 |
| | 1534 | 675 | 4.70 |
| | 1692 | 650 | 5.61 |
| ZrC (103.23) | 0 | 613 | 0.172×10^{-18} |
| | 298 | 605 | 0.757 |
| | 1105 | 600 | 2.59 |
| | 1373 | 580 | 3.42 |
| | 1703 | 580 | 4.24 |
| | 1973 | 570 | 5.065 |

TABLE 1.- CALCULATED VALUES OF MEAN SQUARE VIBRATIONAL AMPLITUDE
AT VARIOUS TEMPERATURES FROM DEBYE CHARACTERISTIC TEMPERATURES -

Concluded

| Material | T, °K | θ , °K | μ^2 , cm ² |
|-----------------|-------|---------------|---------------------------|
| ZrN (105.23) | 0 | 541 | 0.191×10^{-18} |
| | 298 | 540 | 0.922 |
| | 1030 | 520 | 3.135 |
| | 1288 | 520 | 3.96 |
| | 1539 | 518 | 4.75 |
| | 1699 | 518 | 5.24 |

TABLE 2.- CALCULATED VALUES OF THE FACTOR z^2
FROM THE CURVES OF FIGURE 9

| Material | Lattice parameter, | r_0^2 | rz^2 | r | z^2 |
|--------------------------------|-----------------------|-------------------------------------|--------|------|-------|
| (lattice system) | \AA | $\frac{\text{\AA}^2}{\text{\AA}^2}$ | | | |
| Aluminum (f.c.c.) | 4.049 | 6.50 | 14.68 | 2.17 | 6.75 |
| Copper (f.c.c.) | 3.614 | 5.18 | 13.22 | 1.96 | 6.75 |
| Iron (b.c.c.) | 2.866 | 5.17 | 14.95 | 1.60 | 9.35 |
| Gold (f.c.c.) | 4.078 | 6.60 | 13.16 | 3.03 | 4.34 |
| Lead (f.c.c.) | 4.941 | 9.40 | 6.76 | 2.37 | 2.48 |
| Silver (f.c.c.) | 4.078 | 6.60 | 13.76 | 2.40 | 5.74 |
| Tungsten (b.c.c.) | 3.165 | 6.32 | 16.40 | 1.62 | 10.12 |
| Titanium carbide (NaCl) | 4.326 | 4.69 | 15.10 | * | |
| Titanium nitride (NaCl) | 4.242 | 4.50 | 13.79 | * | |
| Zirconium carbide (NaCl) | 4.696 | 5.51 | 15.10 | * | |
| Zirconium nitride (NaCl) | 4.575 | 5.28 | 16.38 | * | |

*These values not available.

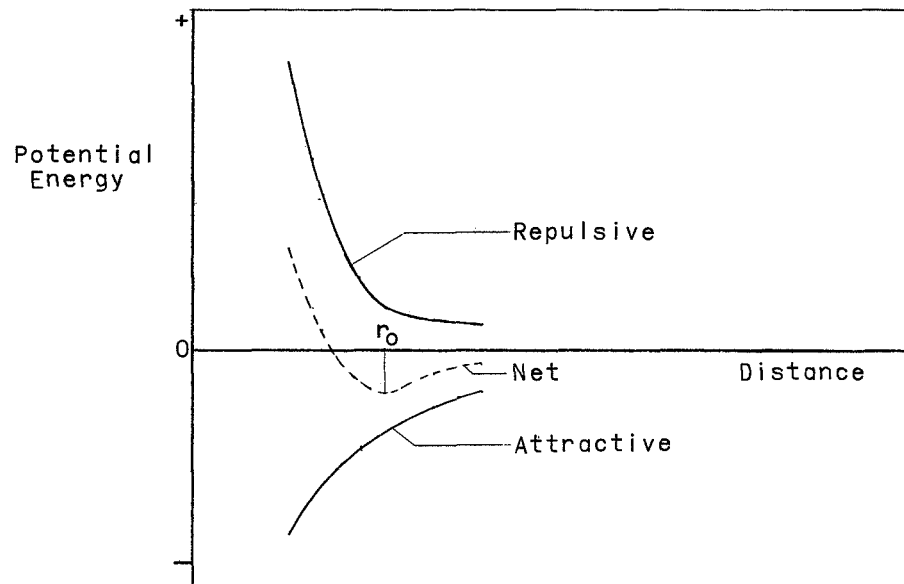


Figure 1.- Potential energy relationships for a pair of atoms.

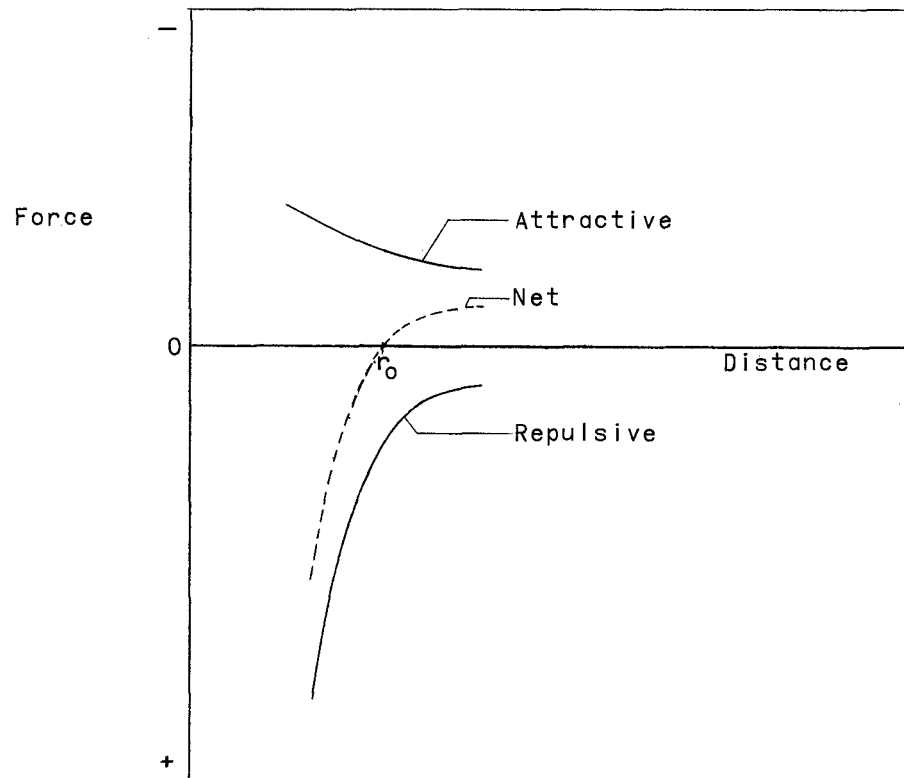


Figure 2.- Force relationships for a pair of atoms.

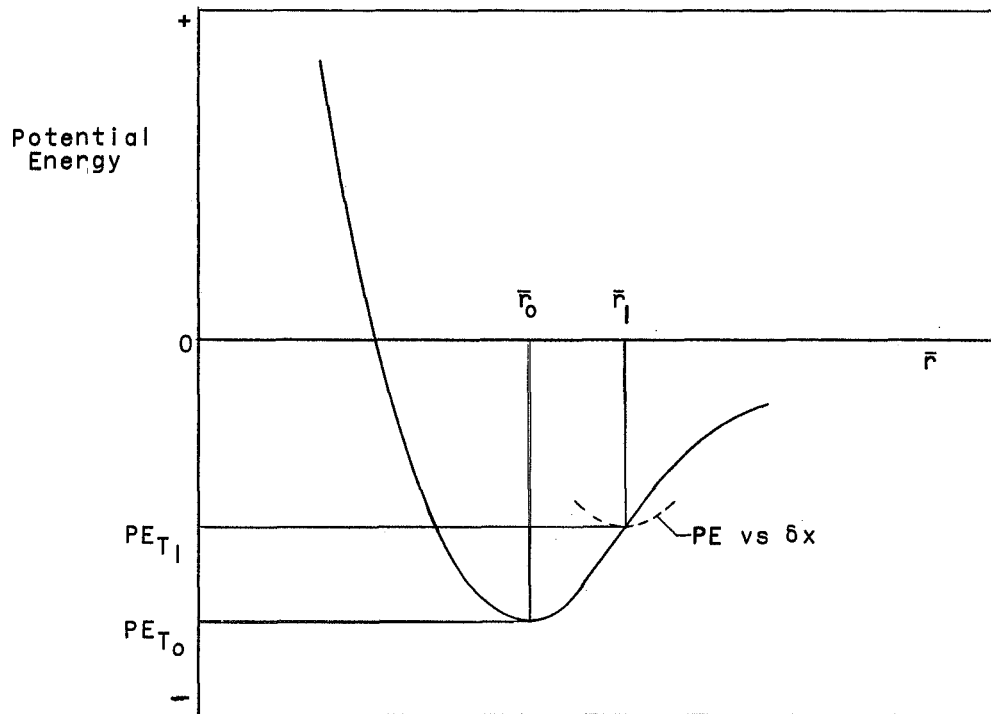


Figure 3.- Potential energy versus δx curve superimposed on the curve of the potential energy of the crystalline solid as a function of the mean distance between atoms, \bar{r} . (The scale of the former curve is magnified over that of the latter curve, for clarity.)

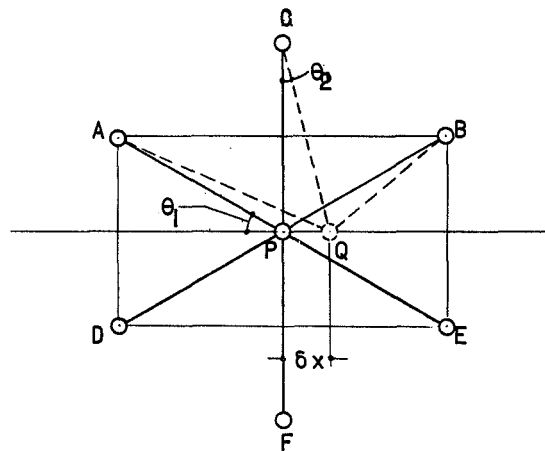


Figure 4.- Geometrical interpretation of forces between atoms in a lattice when one atom is displaced from its mean position.

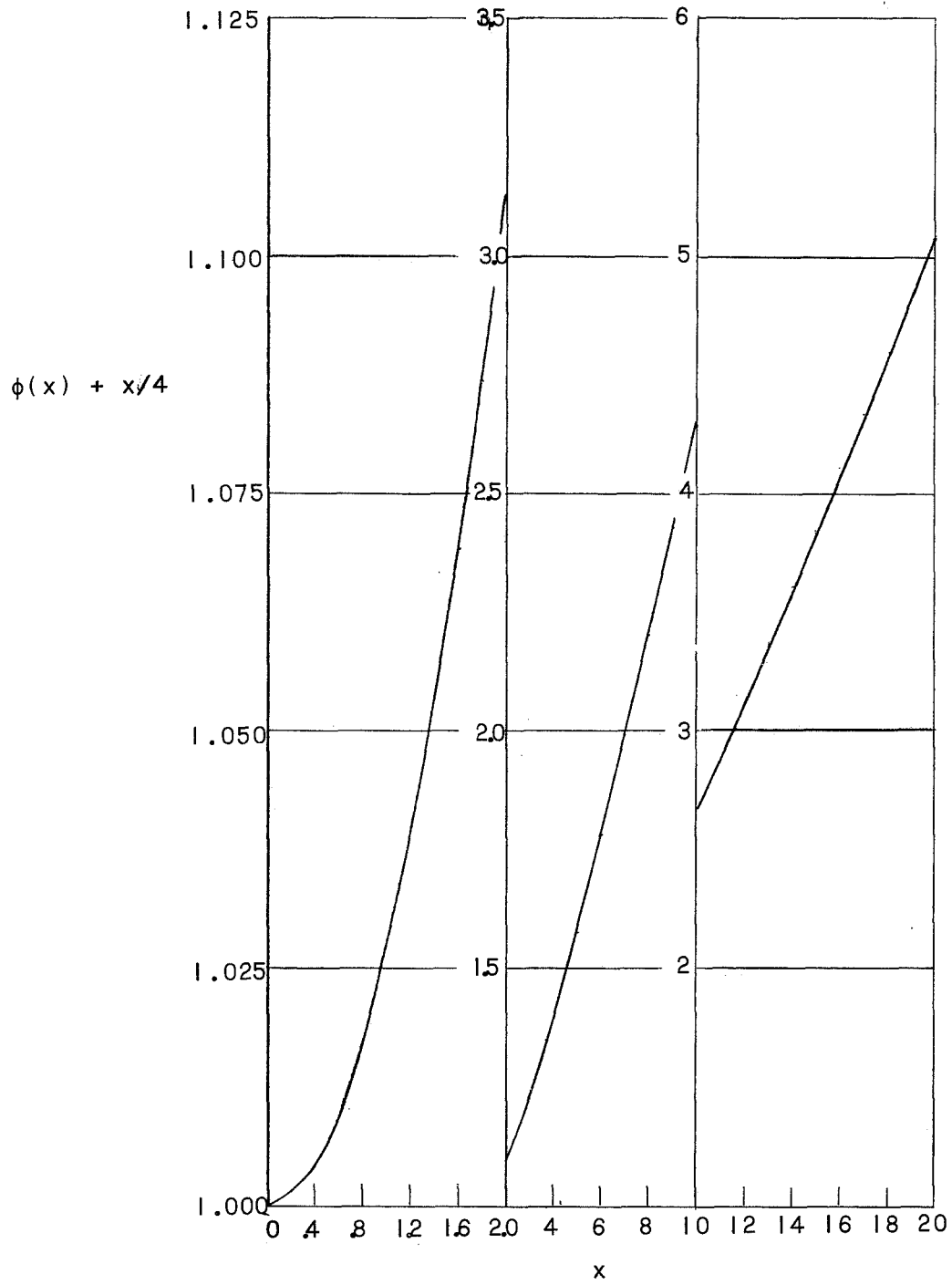


Figure 5.- The function $\left\{ \phi(x) + x/4 \right\}$ versus x , where $x = \Theta/T$.

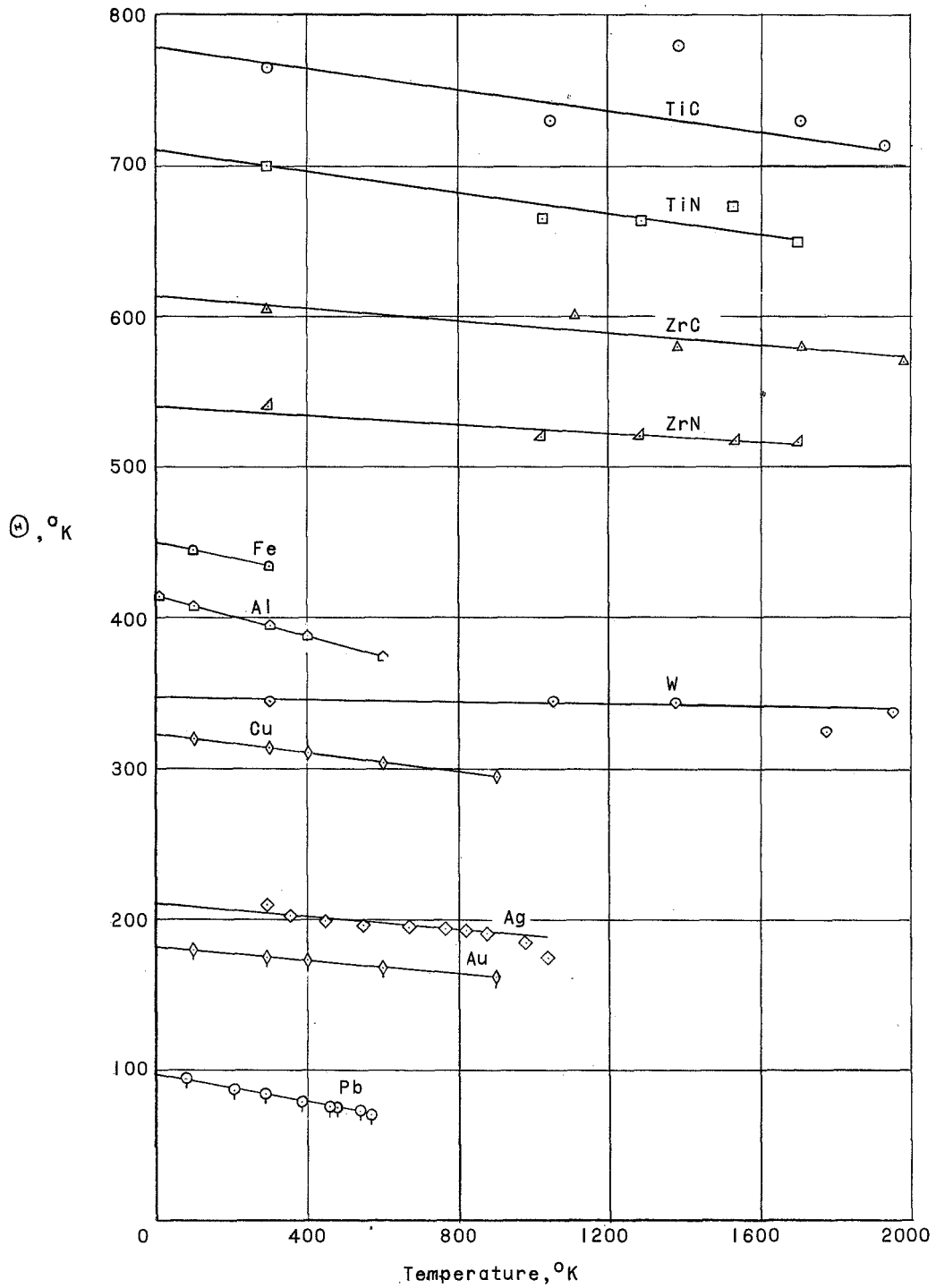


Figure 6.- Variation of Debye characteristic temperature with temperature for several metals and compounds.

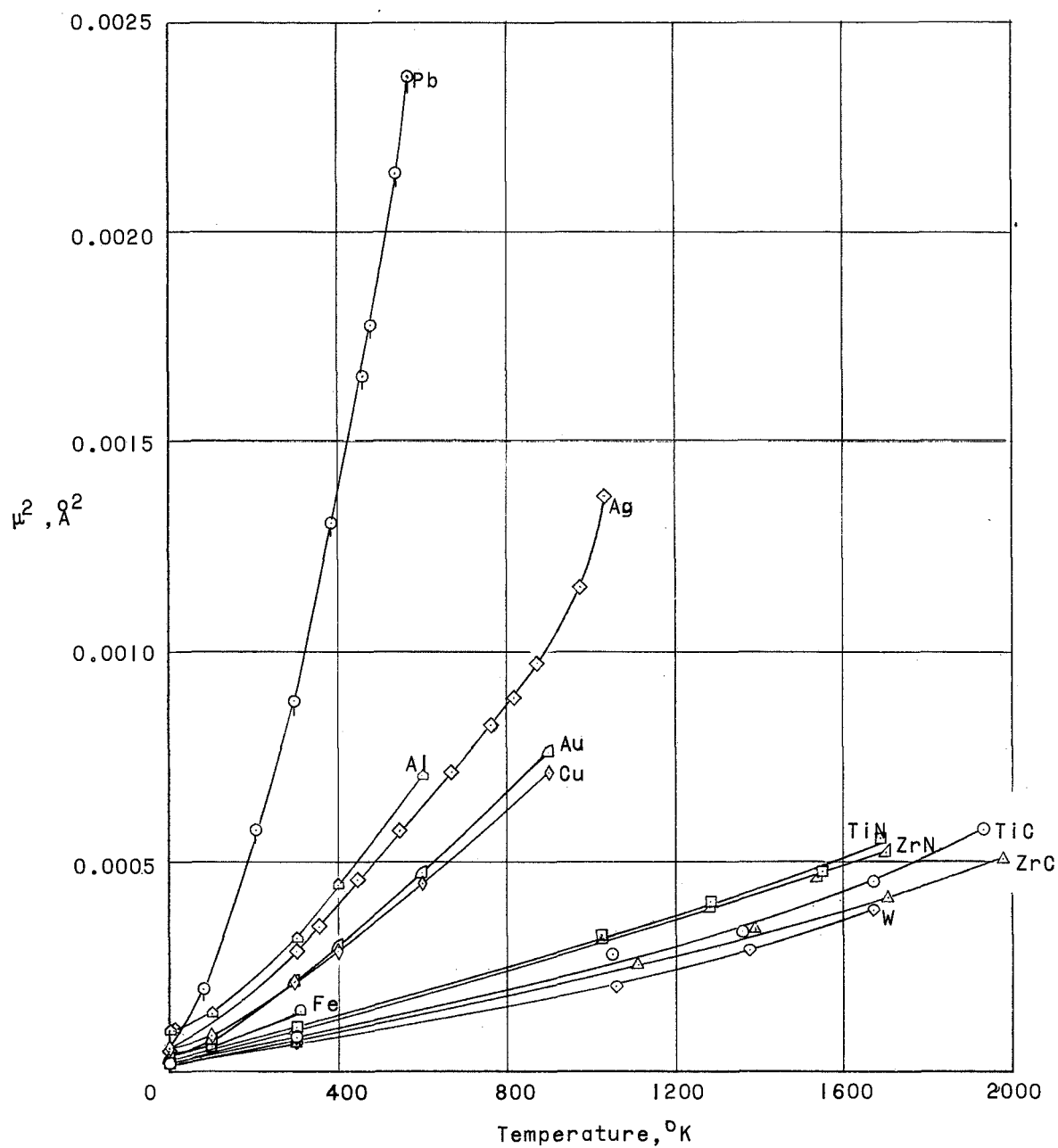


Figure 7.- Variation of mean square vibrational amplitude with temperature for several metals and compounds.

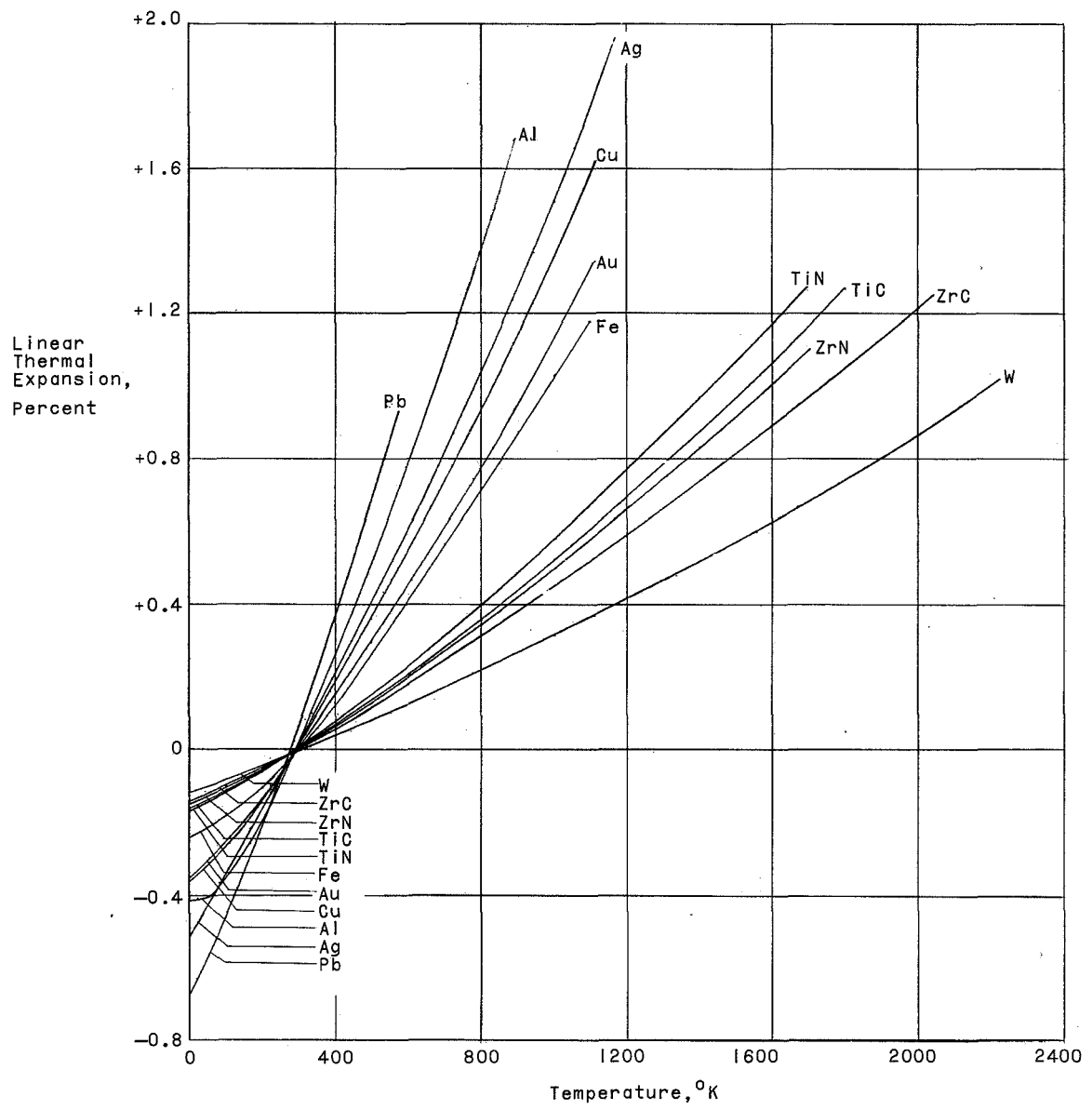


Figure 8.- Variation of linear thermal expansion with temperature for several metals and compounds.

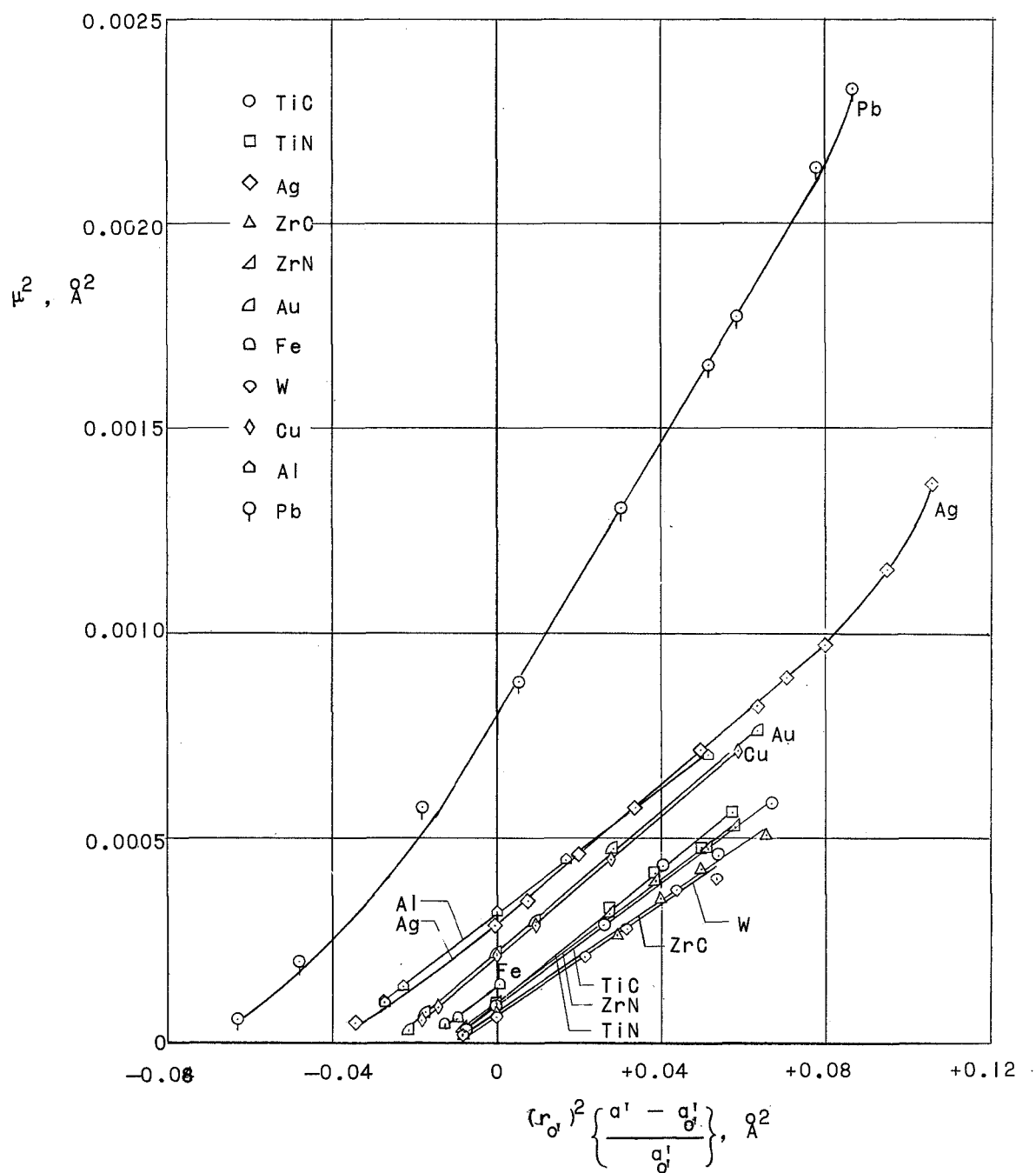


Figure 9.- Variation of mean square vibrational amplitude with the product of linear thermal expansion and r^2 for several metals and compounds.